Journal of Membrane Science 401–402 (2012) 97–108

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Characterization and gas permeability of polyurethane and polyvinyl acetate blend membranes with polyethylene oxide–polypropylene oxide block copolymer

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ARTICLE INFO

Article history:
Received 24 October 2011
Received in revised form 2 January 2012
Accepted 28 January 2012
Available online 6 February 2012

Keywords:
Polyurethane
Polyvinyl acetate
Block copolymer
Membrane
Gas separation

ABSTRACT

Blend membranes of polyurethane (PU) and polyvinyl acetate (PVAc) were prepared in the presence of various polyethylene oxide–polypropylene oxide–polyethylene oxide triblock copolymer (Pluronic) contents by solution casting technique with N,N-dimethylformamide as solvent. The blends with 5% (wt) PVAc showed higher CO_2 permeability (≈73 Barrer) compared to the PU membrane. The domain size of the dispersed PVAc phase of PU/PVAc blend membranes was controlled by adding the Pluronic. When the Pluronic was added at 0.5–2 parts per hundred of PU/PVAc blend (phr) in PU/PVAc membranes in the range of the PVAc content of 5–15% (wt), the domain size of the dispersed phase was reduced markedly and its permeability was consequently increased. In the blend membranes with 2–4 phr Pluronic contents an enhancement of CO_2/CH_4 ($\alpha \approx 33$) and CO_2/N_2 ($\alpha \approx 97$) selectivities was observed. According to thermal analysis, these results were attributed to the presence of ethylene oxide–propylene oxide units which increase CO_2 permeability and to a decrease of crystallinity in PU/PVAc blends. The experimental permeabilities of the blends were compared with the calculated permeabilities based on modified additive logarithmic model.

1. Introduction

Applications of polymeric membranes as gas separation membranes are used in a wide variety of areas such as air separation, separation of carbon dioxide from natural gas and removal of hydrogen from mixture with hydrocarbons in petrochemical processing [1].

Mixing different polymers to achieve a membrane material with superior properties to those of the initial constituting components has been used as an attractive method to achieve better separation characteristics in membrane materials [2–6]. Moreover, the use of polymer blends allows the easy control of their gas transport properties by adjusting the composition ratio and micro-structure of their constituting polymers [5]. Gas permselectivity through miscible polymer blends is reported to vary monotonically between those of pure polymers. However, the permselectivity through immiscible blend membranes strongly depends on the membrane morphology, the specific volume fraction and the size and the shape of the dispersed and continuous phases [7]. The effect of the volume fraction of the dispersed phase on transport properties of immiscible polymer blends has been widely investigated [3–7]. However, the size and shape effects of micro-phases have not been paid much attention. In most studies on blend membranes, rubbery polymers have been used as the matrix together with the glassy polymers. This allows combining the high permeability of the former with high selectivity of the latter and achieving a better membrane material [6,8]. Polyurethanes (PU) have been accepted as elastomers with good membrane-forming ability, high flexibility and gas permeability. However, the use of PU membranes for gas separation is limited by their low selectivity [9–11]. Polyvinyl acetate (PVAc) as a glassy polymer seems to be one of the most interesting compounds for blending due to its polarity and CO_2 affinity among the other suggested polar structures. The interaction between the residual carbonyl groups on the polar gases, such as CO_2, and the morphological changes may lead to an increase of solubility associated with an increase of Henry's contribution [12,13].

Morphology of an immiscible blend of two polymers strongly depends upon their composition. At a given composition, the size of the dispersed phase can also be varied by adding a block copolymer compatibilizer. A block copolymer has been commonly employed as a compatibilizer to control the size of the dispersed phase where each block is miscible with one or the other phase of the polymer blends. Such block copolymer in a polymer blend migrates and locates between two phases, if its concentration is lower than its critical micelle concentration [14]. The migration of the

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doi:10.1016/j.memsci.2012.01.035

block copolymer is due to the thermodynamic energy balance by enthalpic gain and entropic loss. When the block copolymer stays in the interphase, the interfacial tension of the interphase will be reduced and consequently the dispersed phase becomes finer [14]. Polyethylene oxide (PEO) was found to be miscible with most ethylene-based polymers [15–19]. Similarly, partial miscibility was observed in blending polymethyl methacrylate and polyvinyl acetate with poly(propylene oxide-b-ethylene oxide), which was attributed to the entropic factor and the hydrogen bonding with the hydroxyl end groups [20,21]. Block copolymers based on poly(ethylene oxide) (PEO) also exhibit excellent CO_2 permeability and can effectively separate CO_2 from other gases [22].

In this work we have studied the gas-permeation and thermal properties of the PU/PVAc/Pluronic blends. In particular, we have studied the effect of the amount of PVAc and Pluronic on permeability of gases through the blends. Furthermore, we discuss the effect of polymeric composition on the CO_2/N_2, CO_2/O_2, CO_2/CH_4 and O_2/N_2 selectivities. Finally, the experimental permeability was compared with that calculated on the basis of blend composition.

2. Background

The permeability of the gas A, through membranes was determined using the following equation:

$$P = \frac{q\ell}{A(p_1 - p_2)} \tag{1}$$

where P is permeability expressed in Barrer (1 Barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cm-Hg), q is the flow rate of the permeate gas passing through the membrane (cm^3/s), ℓ is the membrane thickness (cm), p_1 and p_2 are the partial pressures of feed side and permeate side, respectively (cm-Hg) and A is the effective membrane area (cm^2).

If the diffusion process obeys Fick's law, and the downstream pressure is much less than the upstream pressure, the permeation coefficient of gas A is given by:

$$P_A = S_A \cdot D_A \tag{2}$$

where D_A is the average effective diffusivity through the film, and S_A is the apparent sorption coefficient.

The ideal selectivity, $\alpha_{A/B}$ (the ratio of single gas permeabilities) of membranes was calculated from the pure gas permeation experiments [23]:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \cdot \frac{S_A}{S_B} \tag{3}$$

where D_A/D_B is the diffusivity selectivity, i.e. the ratio of the diffusion coefficients of gases A and B. The ratio of the solubilities of gases A and B, S_A/S_B, is the solubility selectivity.

Diffusivity selectivity is strongly influenced by the size difference between the penetrant molecules and the size-sieving ability of the polymer matrix. Whereas, solubility selectivity is controlled by the relative condensability of the penetrants and the relative affinity between the penetrants and the polymer matrix [24].

The permeability of a two-phase polymer system with weak interactions can be determined with the model proposed by Min and Paul [25]. Also applied by other groups [26–28], it considers the permeability of the pure gases in the constituting polymers following a logarithmic additive rule such as:

$$\text{Ln } P_{\text{blend}} = \varphi_1 \text{Ln}(P_1) + \varphi_2 \text{Ln}(P_2) \tag{4}$$

where P_{blend} is the blend gas permeability, φ_1 and φ_2 are the volume fractions of polymer 1 and 2 in the blend, and P_1 and P_2 are the permeabilities of the pure polymers 1 and 2.

We turned our attention to the interfacial block copolymer phase, the Pluronic zones that exist between the pure micro-phases of PU and PVAc. A model was adopted which treats the interfacial regions as a distinct third phase in the blend. Eq. (4) was modified to account for this third phase:

$$\text{Ln } P_{\text{blend}} = \varphi_1 \text{Ln}(P_1) + \varphi_2 \text{Ln}(P_2) + \varphi_3 \text{Ln}(P_3) \tag{5}$$

where φ_3 and P_3 are the volume fraction and permeability of the interfacial region, related to the block copolymer.

Gas transport properties in a semi-crystalline polymer are usually modeled assuming that the crystals act as an impermeable dispersed phase imbedded in an amorphous phase. Models are then developed for the influence of crystallinity on solubility and diffusivity. In a rubbery polymer, the effect of crystallinity on penetrant sorption is typically represented as follows [24]:

$$S_A = S_{A,a}\varphi_a \tag{6}$$

where S_A is the observed solubility coefficient, $S_{A,a}$ is the solubility coefficient in the amorphous polymer, and φ_a is the amorphous phase volume fraction. The influence of crystallinity on diffusivity is commonly described as follows [24]:

$$D_A = \frac{D_{A,a}}{\tau\gamma} \tag{7}$$

where $D_{A,a}$ is the diffusion coefficient in the amorphous polymer, τ is a tortuosity factor, and γ is the effective chain immobilization factor. τ characterizes the tortuosity of the amorphous phase caused by the presence of dispersed impermeable crystallites. Simple models from composites theory, such as the one given below, are often used to describe the influence of crystallinity on tortuosity [24]:

$$\tau = \frac{1}{\varphi_a} \tag{8}$$

The effective chain immobilization factor, γ, accounts for the restricted segmental mobility in the amorphous phase by crystallites and reduced fractional free volume. By using Eqs. (6)–(8), the gas permeability is calculated by [24]:

$$P_A = P_{A,a} \cdot \frac{\varphi_a^2}{\gamma} \tag{9}$$

3. Experimental

3.1. Materials

Polytetramethylene ether glycol (PTMEG, M_w = 2000 g mol^{-1}), PVAc (M_w = 100,000 g mol^{-1}) and the PEO–PPO–PEO triblock copolymers with the average composition $EO_{97}PO_{68}EO_{97}$ (Pluronic), and a nominal molar mass of 12,600 g mol^{-1} were obtained from Sigma–Aldrich. PTMEG was dried at 80 °C under vacuum for 48 h in order to remove the residual water. 1,4-Butanediol (BDO), Toluene diisocyanate (TDI) and N,N-dimethylformamide (DMF) were purchased from Merck. The chain extender (BDO) was dried over 4 Å molecular sieves before use. CO_2, N_2 and O_2 gases (purity 99.99%) used for gas permeation tests were purchased from Roham Gas Co. (Tehran, Iran) and CH_4 (purity 99.9%) was obtained from Air Products Co. (Tehran, Iran).

3.2. Polymer synthesis

Polyurethane was synthesized by bulk two-step polymerization method [9]. PTMEG was incubated with TDI for 2 h at 85–90 °C under nitrogen atmosphere to obtain macrodiisocyanate prepolymer. The pre-polymer was examined for NCO content using the standard method of n-butyl amine titration (ASTM D2572) [29]. The chain extension of pre-polymer was performed by addition of BDO at room temperature. In order to obtain linear polymer, the molar ratio of NCO:OH was kept at 1:1. The molar ratio of